

REPORT DOCUMENTATION PAGE

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Separate items are enclosed

MEMORANDUM FOR IN-HOUSE PUBLICATIONS

FROM: PROI (TI) (STINFO)

30 Apr 98

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-1998-091

Simon Tam and Mario Fajardo "CO/pH₂ - a Molecular Thermometer"
HEDM Conference Presentation (Statement A)

20021122 006

CO/pH₂ -- a Molecular Thermometer

Simon Tam and Mario E. Fajardo

US Air Force Research Laboratory, Propulsion Directorate
(AFRL/PRSP Bldg. 8451, Edwards AFB, CA 93524-7680)

We utilize reversible temperature dependent changes in the infrared absorption spectrum of CO molecules in solid parahydrogen (pH₂) to probe the temperature profiles of the matrices during deposition. The intensity of a well-resolved absorption feature near 2135 cm⁻¹ shows a monotonic increase with temperature over the 2 to 5 K range. The initial state of this transition is estimated to be 7.9(± 0.5) K above the ground state of CO/pH₂. During the deposition of 100 PPM CO/pH₂ samples, we detect temperature gradients of ~ 10 K/cm in samples subjected to estimated heat loads of ~ 10 mW/cm². The resulting estimated thermal conductivities of ~ 1 mW/cm-K (0.1 W/m-K) are four orders of magnitude lower than the conductivity of single crystal solid pH₂, and more than an order of magnitude lower than previously measured for pH₂ solids doped with 100 PPM concentrations of heavy impurities [V.G. Manzhelli, et al., Low Temp. Phys. v22, p131 (1996)].

DISTRIBUTION STATEMENT A:
Approved for Public Release.
Distribution Unlimited

High Energy Density Matter (HEDM) Cryosolid Propellants

Objectives

- * Trap 5% molar concentration of energetic additives in solid hydrogen.
- * Demonstrate size-scaleable sample production method.

Payoffs

Increased Specific Impulse

$$I_{sp} \propto \sqrt{\Delta H_{sp}}$$

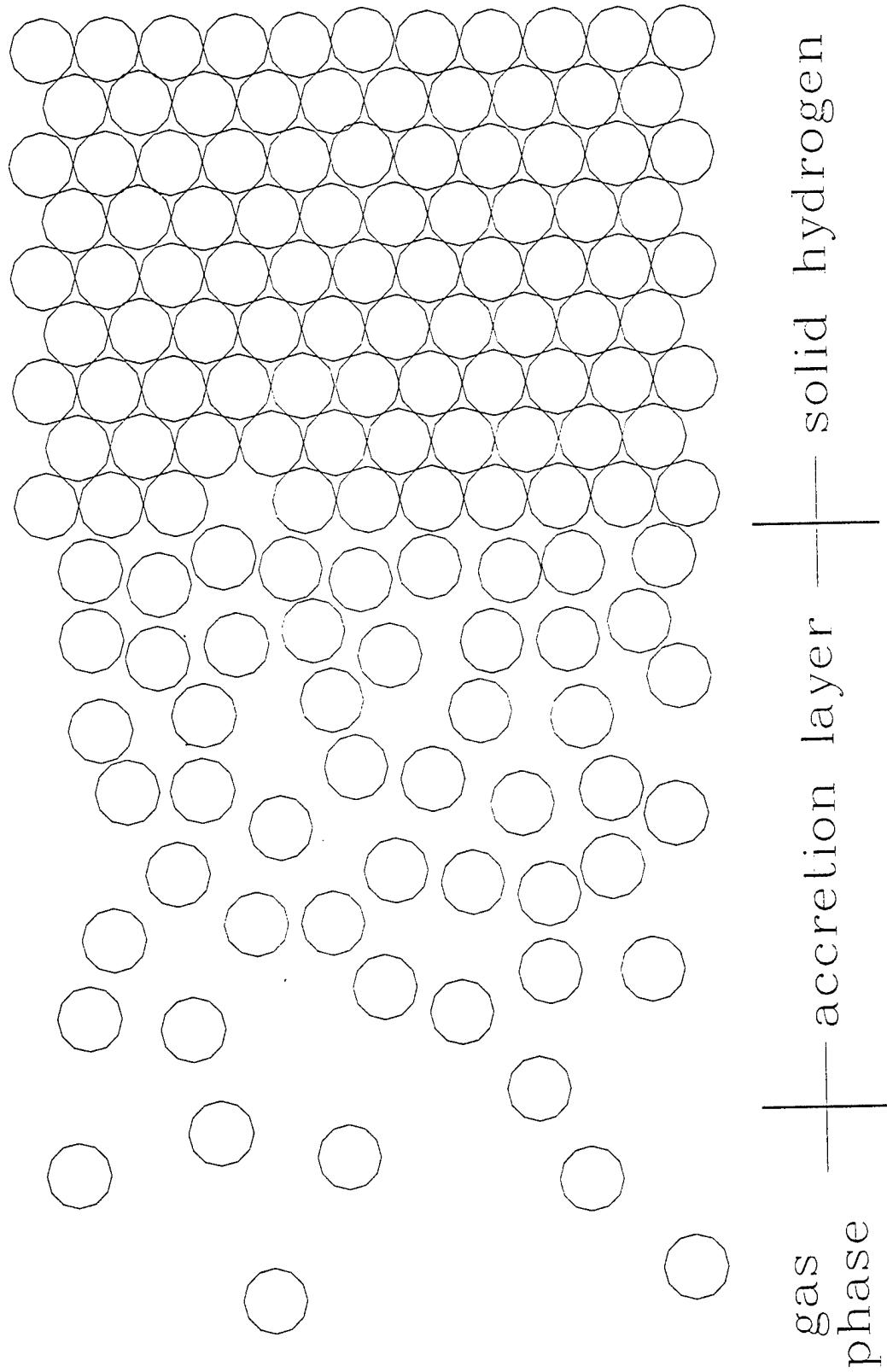
LOX/LH₂ : $I_{sp} = 390$ s
5% B/H₂ + LOX : $I_{sp} = 500$ s (+30%)*

* calculated for $P_{chamber} = 1000$ PSIA, $P_{exhaust} = 14.7$ PSIA

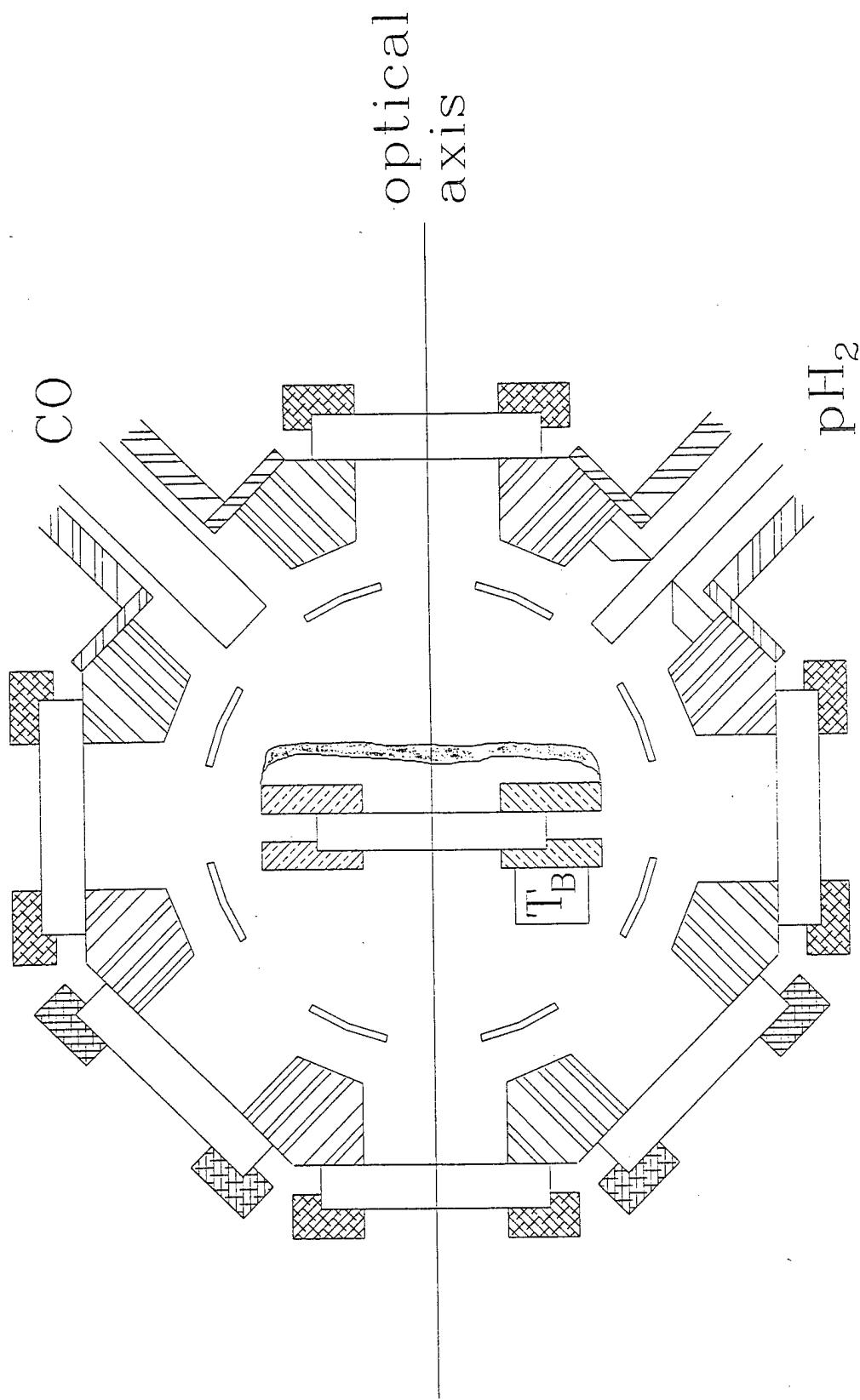
Greater Propellant Density

liquid H₂ : $\rho = 0.070$ g/cm³
solid H₂ : $\rho = 0.087$ g/cm³ (+25%)
50/50 liquid He/solid H₂ : $\rho = 0.105$ g/cm³ (+50%)

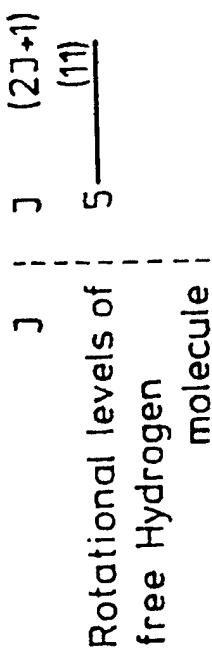
Deposition Cartoon



Experimental Diagram – Sample Deposition



Ortho and Para Hydrogen

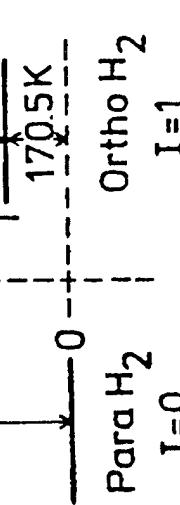
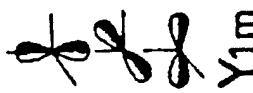


(5) ————— 2

509.9 K

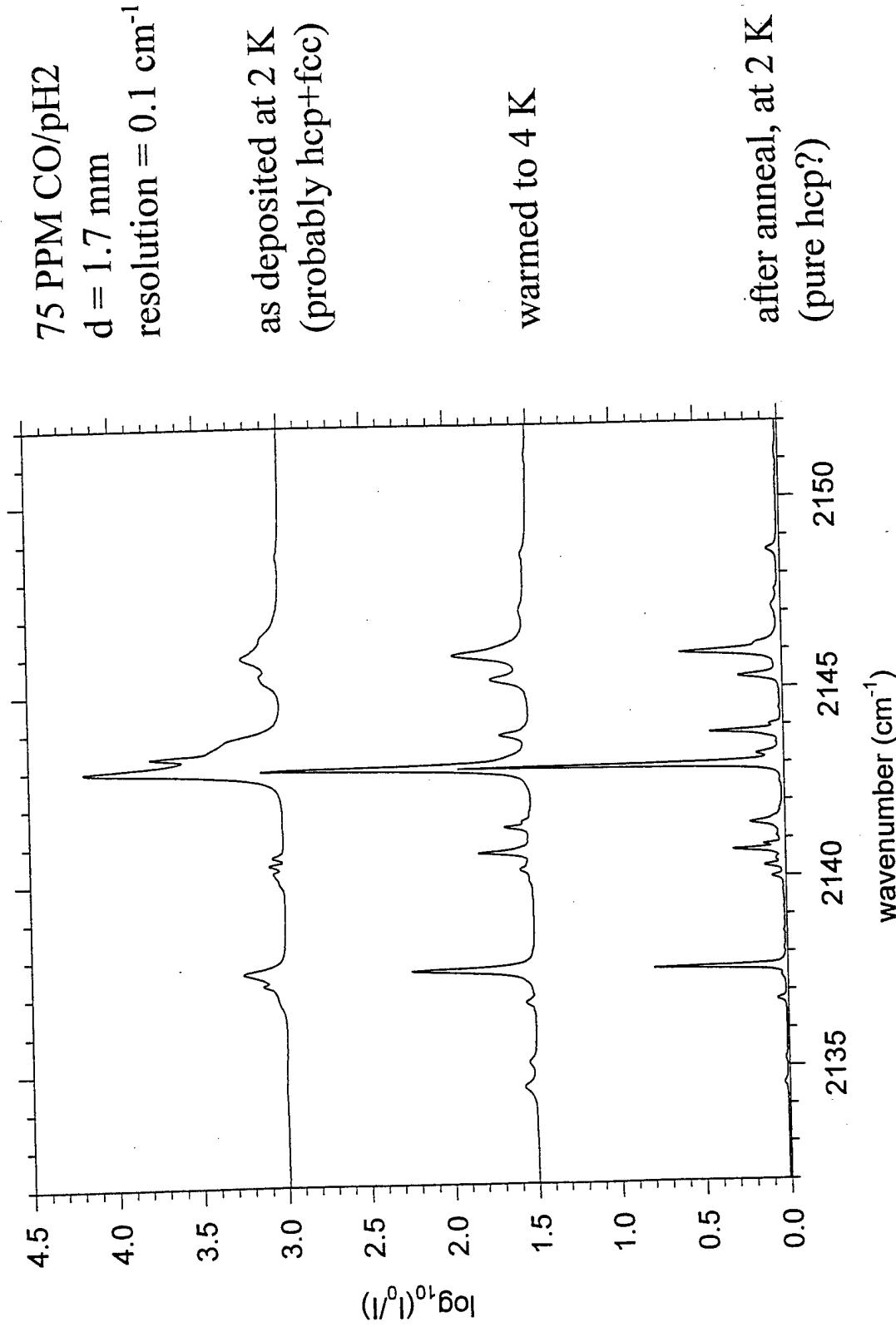
3 ————— (7)

844.7 K

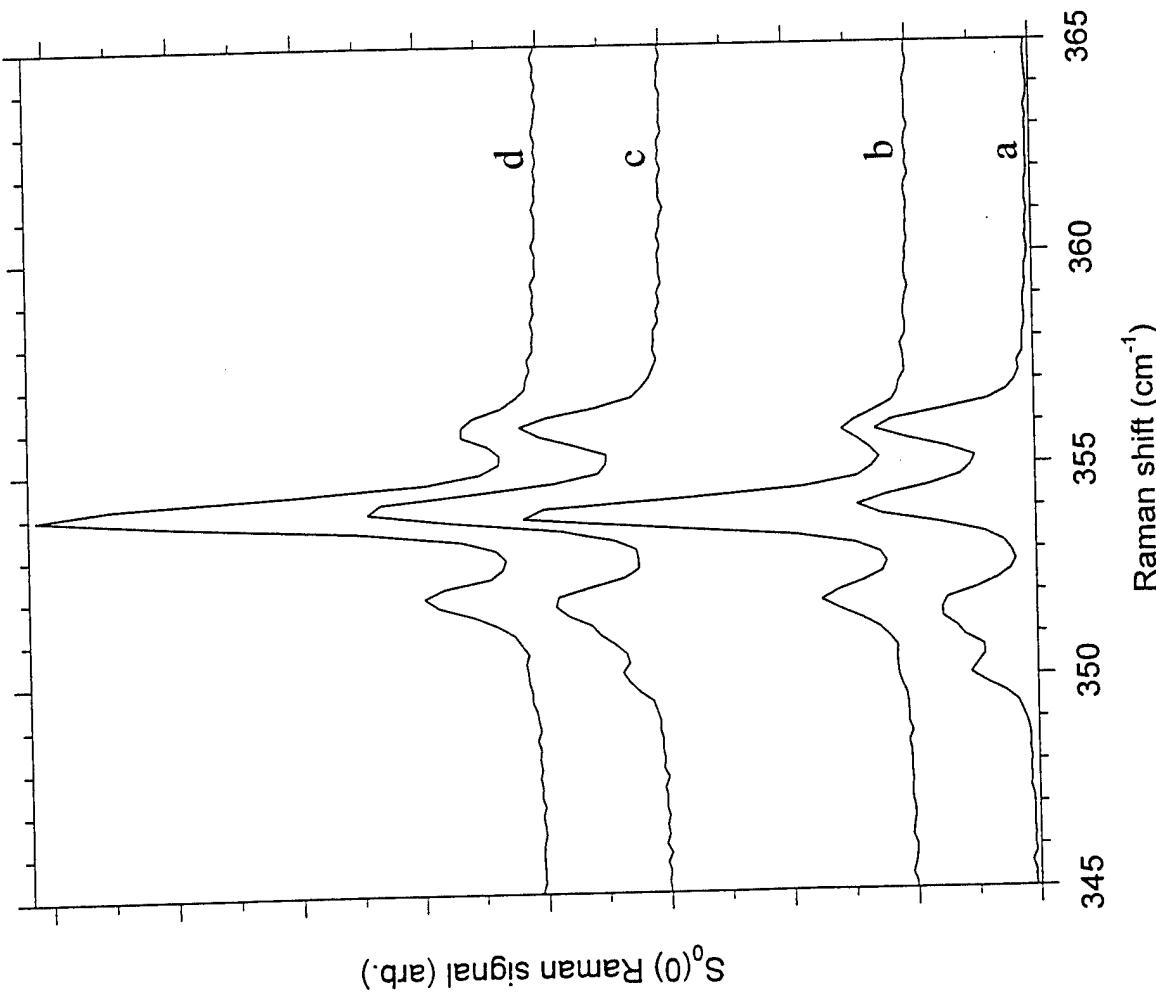


I.F. Silvera,
Rev. Mod. Phys. **52**, 393 (1980).

IR Absorptions of CO/pH₂



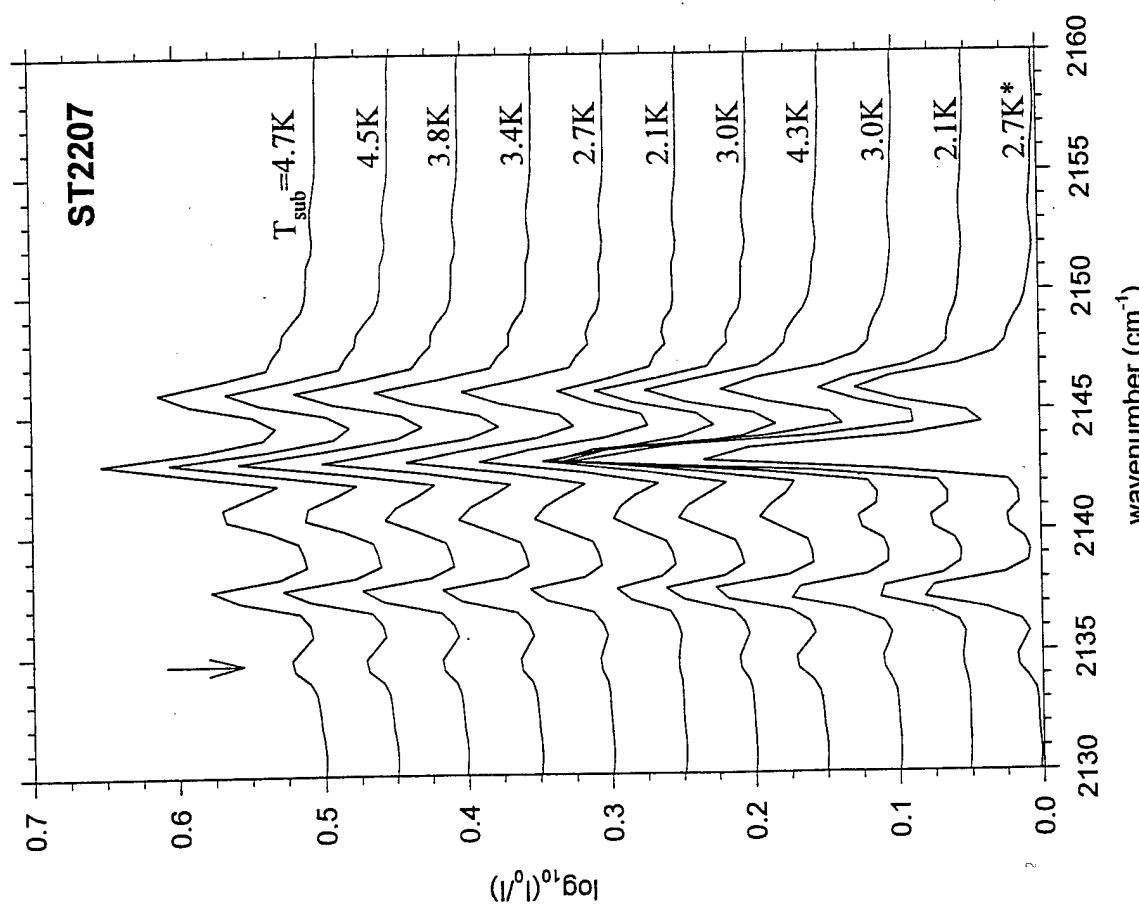
Raman Spectra of 4.5 and 6 mm Thick Parahydrogen Solids



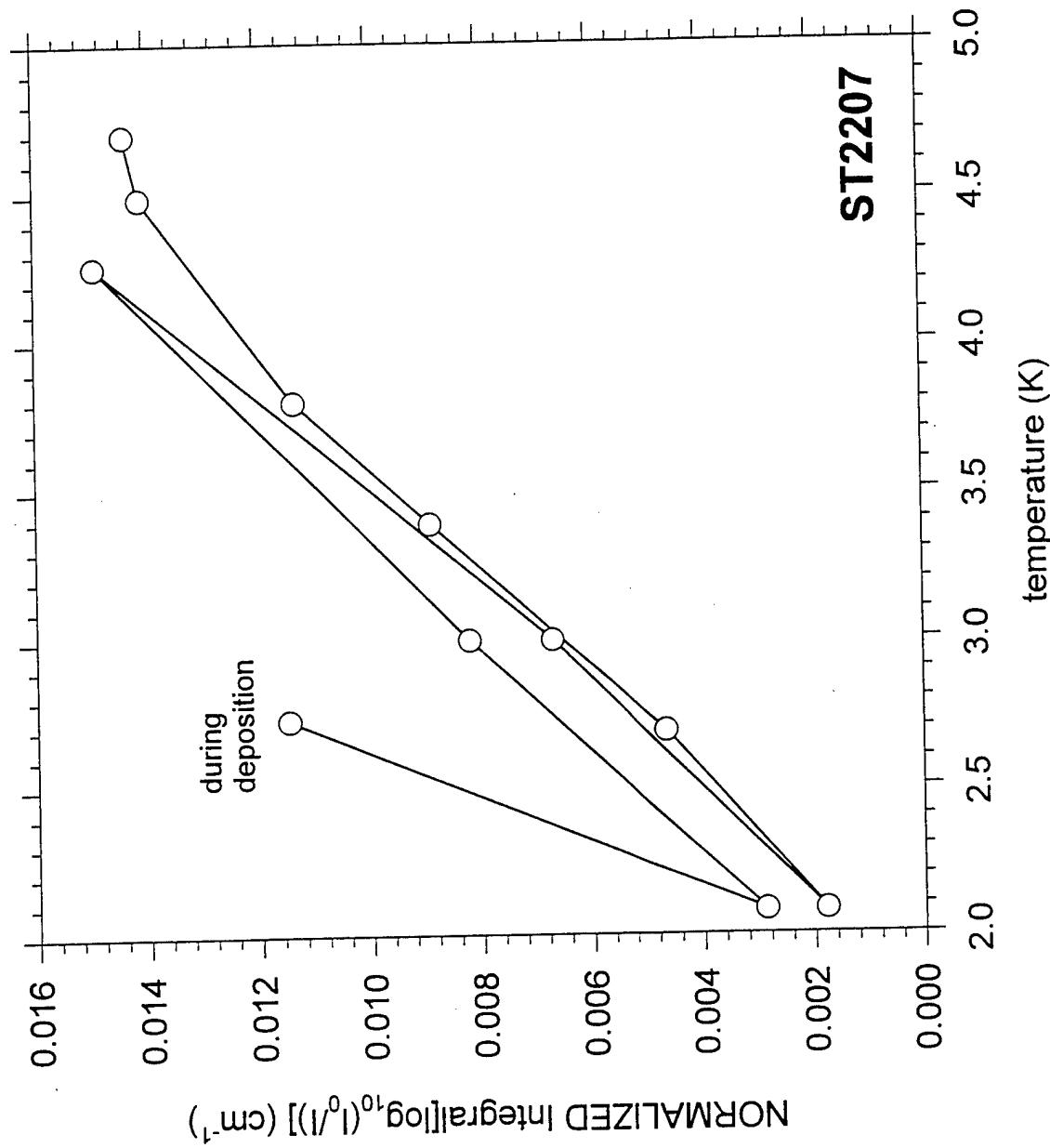
Mixed hcp/fcc as-deposited structure, anneals to hcp;
compare with:

G.W. Collins, et al.,
Phys. Rev. B **53**, 102 (1996).

Reversible Temperature Dependence of CO/pH₂ Spectrum

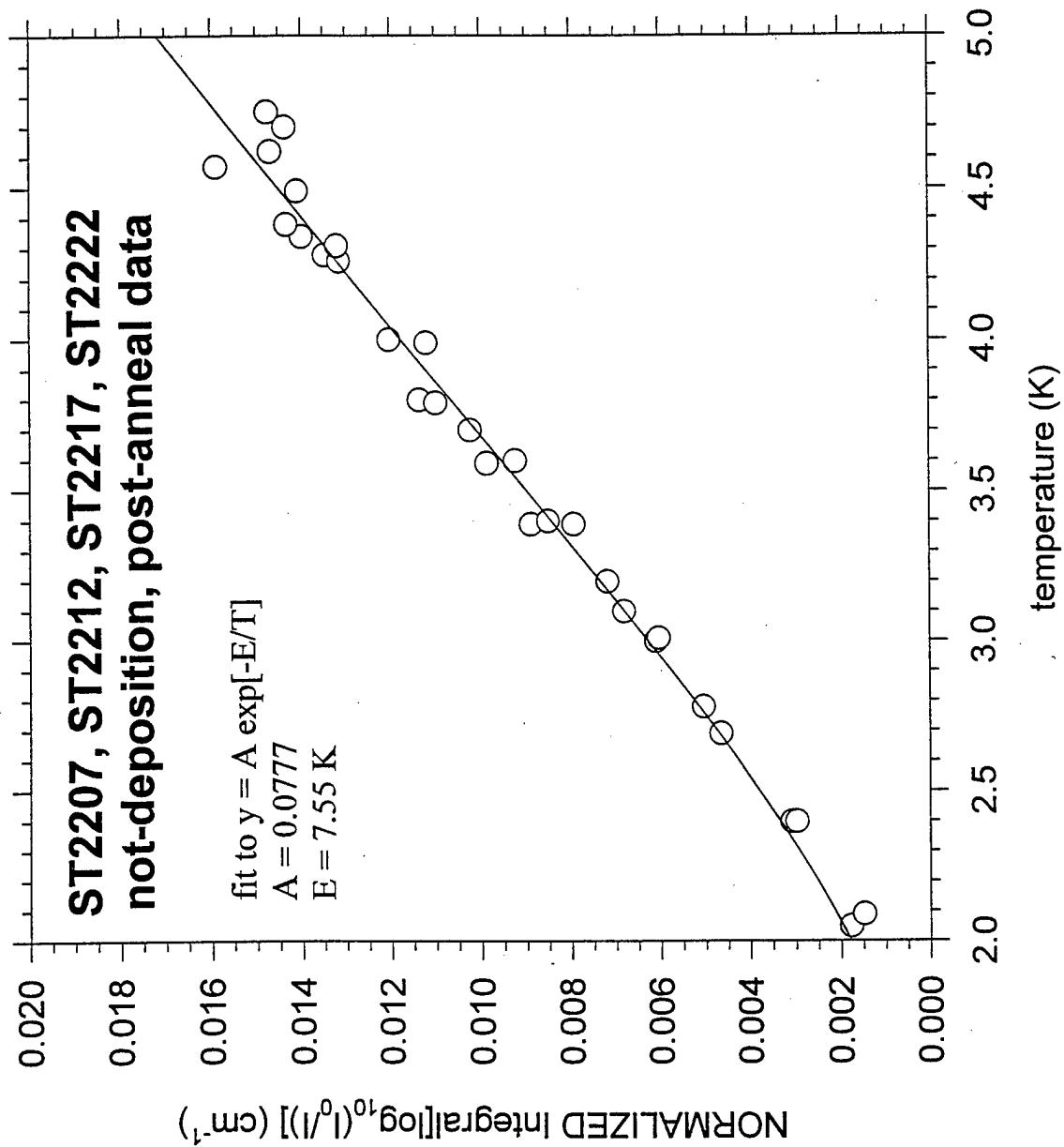


Intensity of 2135 cm^{-1} band vs. Temperature

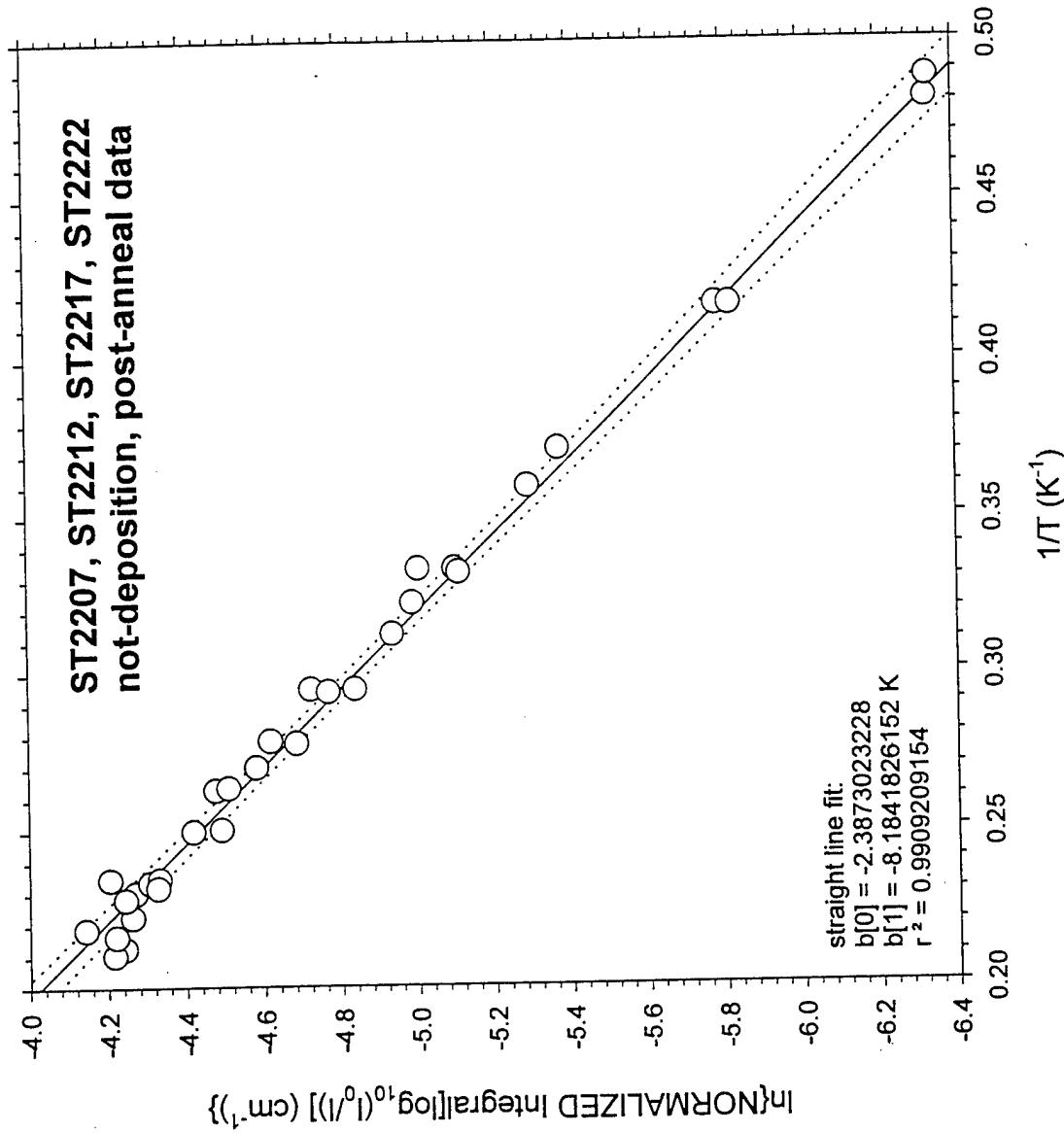


CO/pH₂ Calibration vs. Si Diodes

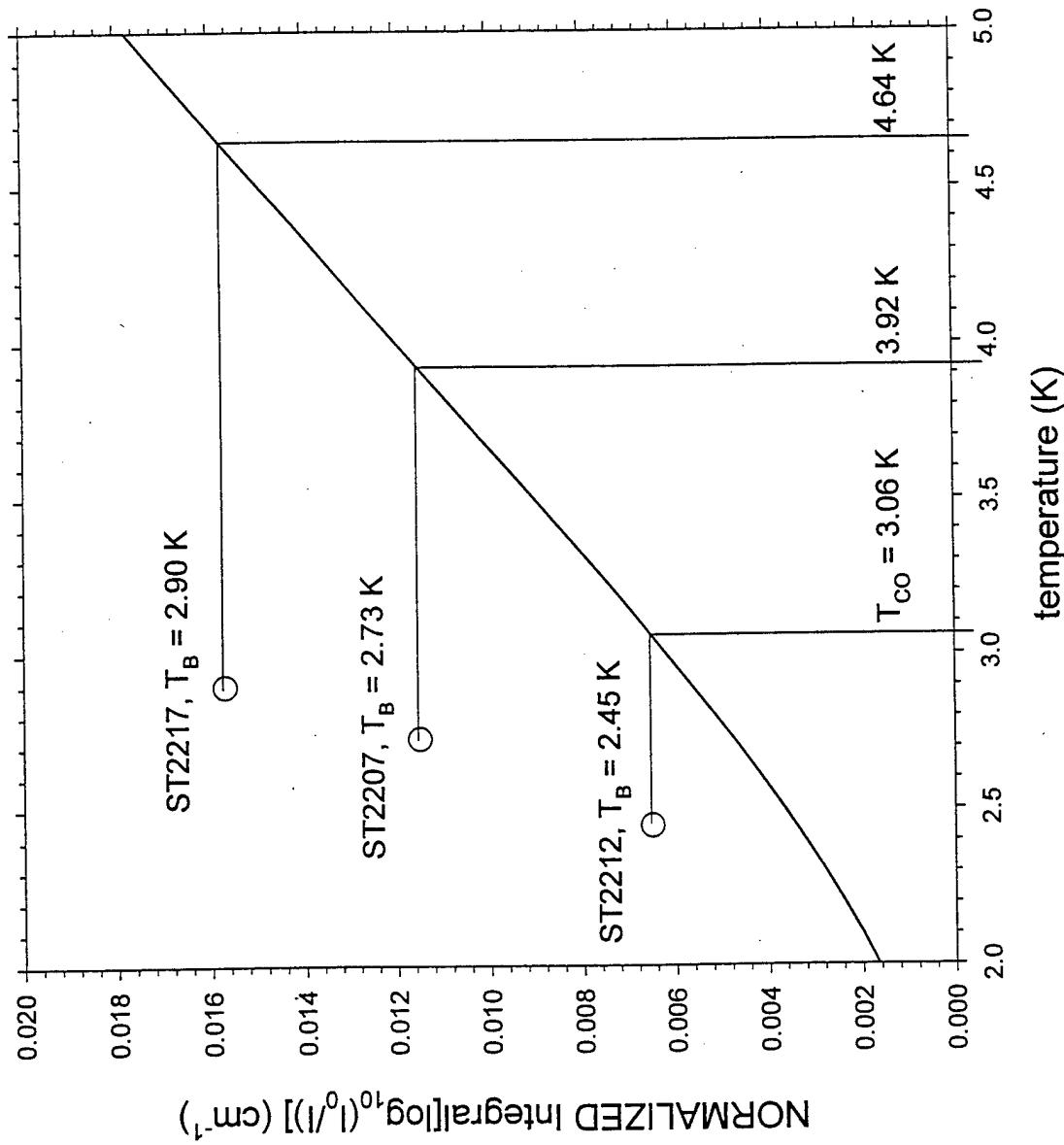
**ST2207, ST2212, ST2217, ST2222
not-deposition, post-anneal data**



“Van’t Hoff Plot”



Substrate and Bulk Hydrogen Temperatures During Deposition



“thermometer curve:”

$$y = A \exp[-E/T]$$

$$A = 0.08602$$

$$E = 7.896 \text{ K}$$

Prior to depositions

$$T_B = 1.89(\pm 0.02) \text{ K}$$

After depositions

$$T_B = 2.08(\pm 0.05) \text{ K}$$

pH₂ inlet & deposition rates:

$$\text{ST2212: } 110 \text{ mmol/hr}$$

$$26 \mu\text{m/min}$$

$$\text{ST2207: } 200 \text{ mmol/hr}$$

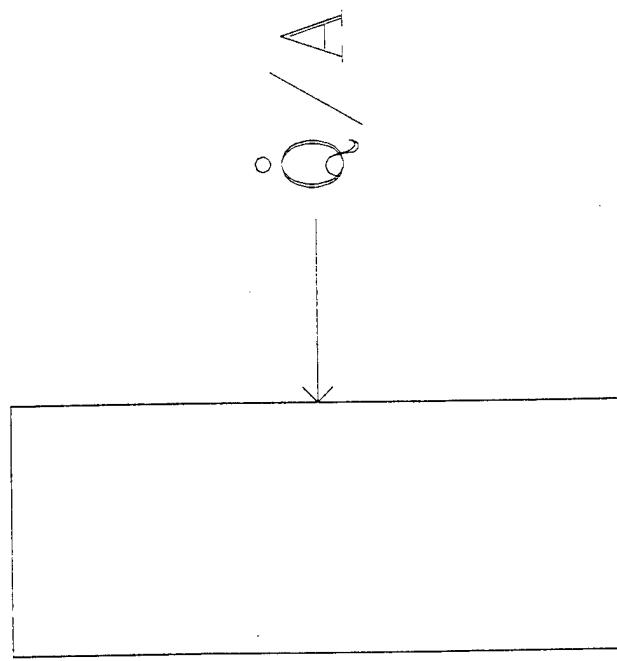
$$48 \mu\text{m/min}$$

$$\text{ST2217: } 240 \text{ mmol/hr}$$

$$55 \mu\text{m/min}$$

1-D Heat Transfer

$$T_{lo} \quad T_{hi}$$



$$\dot{Q}/A = -\kappa \Delta T/\Delta x$$

$$\Delta T = T_{hi} - T_{lo}$$

κ is the thermal conductivity

units:

$$\overset{\circ}{Q} / A$$

$$\dot{Q}/A \text{ (mW/cm}^2)$$

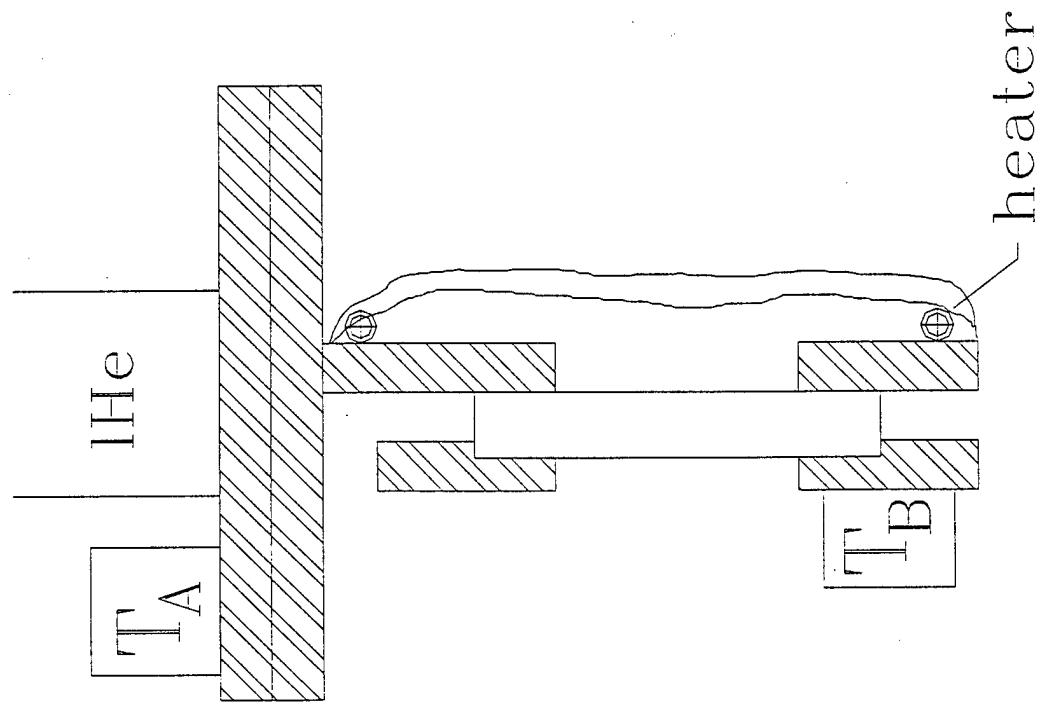
$$\Delta T \text{ (K)}$$

$$\Delta x \text{ (cm)}$$

$$\kappa \text{ (mW/cm-K)}$$

note: 1 mW/cm-K = 0.1 W/m-K

Experimental Diagram – Heat Flux Calibration

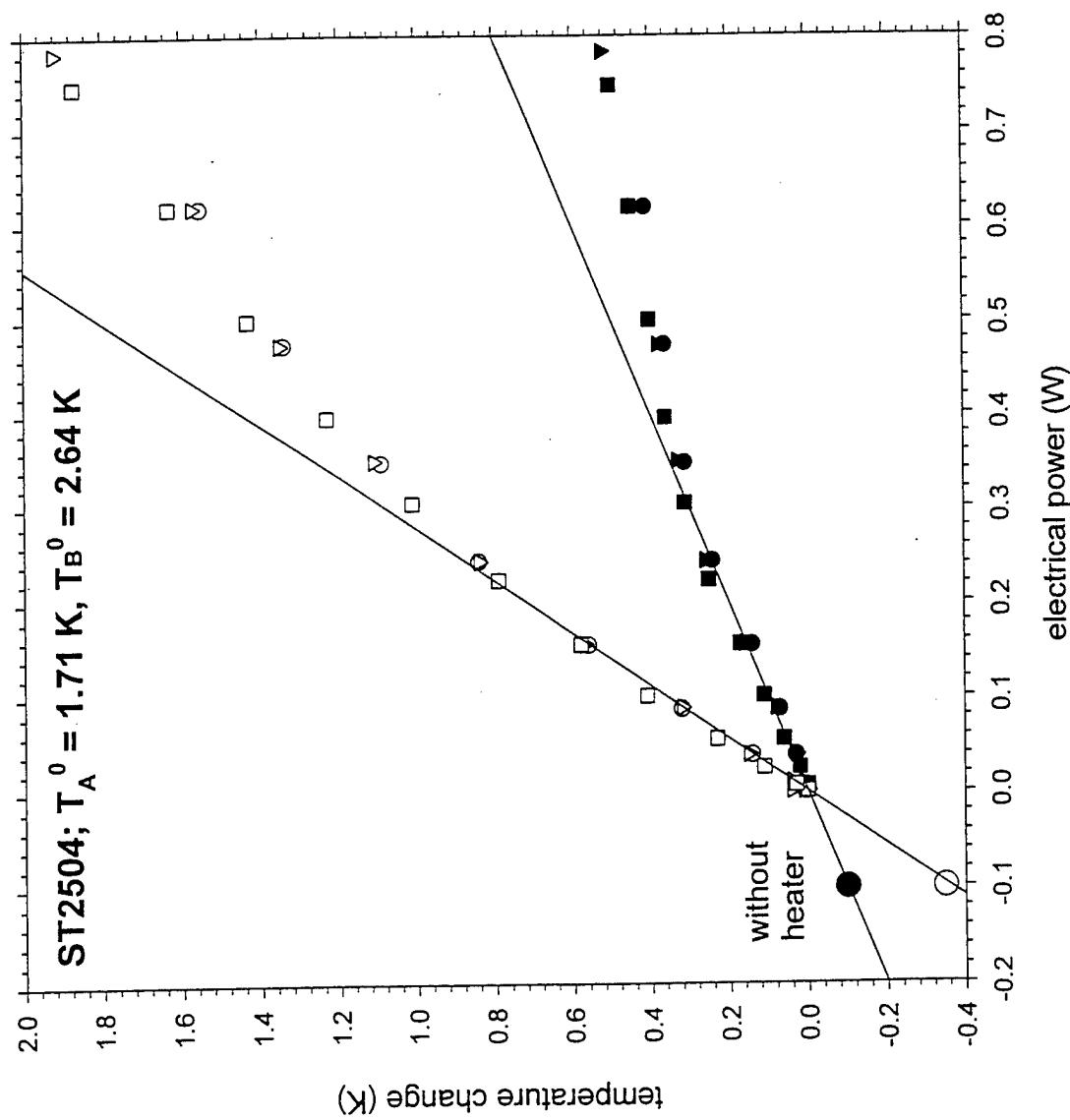


Mimic deposition heat load on substrate holder by using an electrical heater (loop of nichrome wire glued to substrate holder).

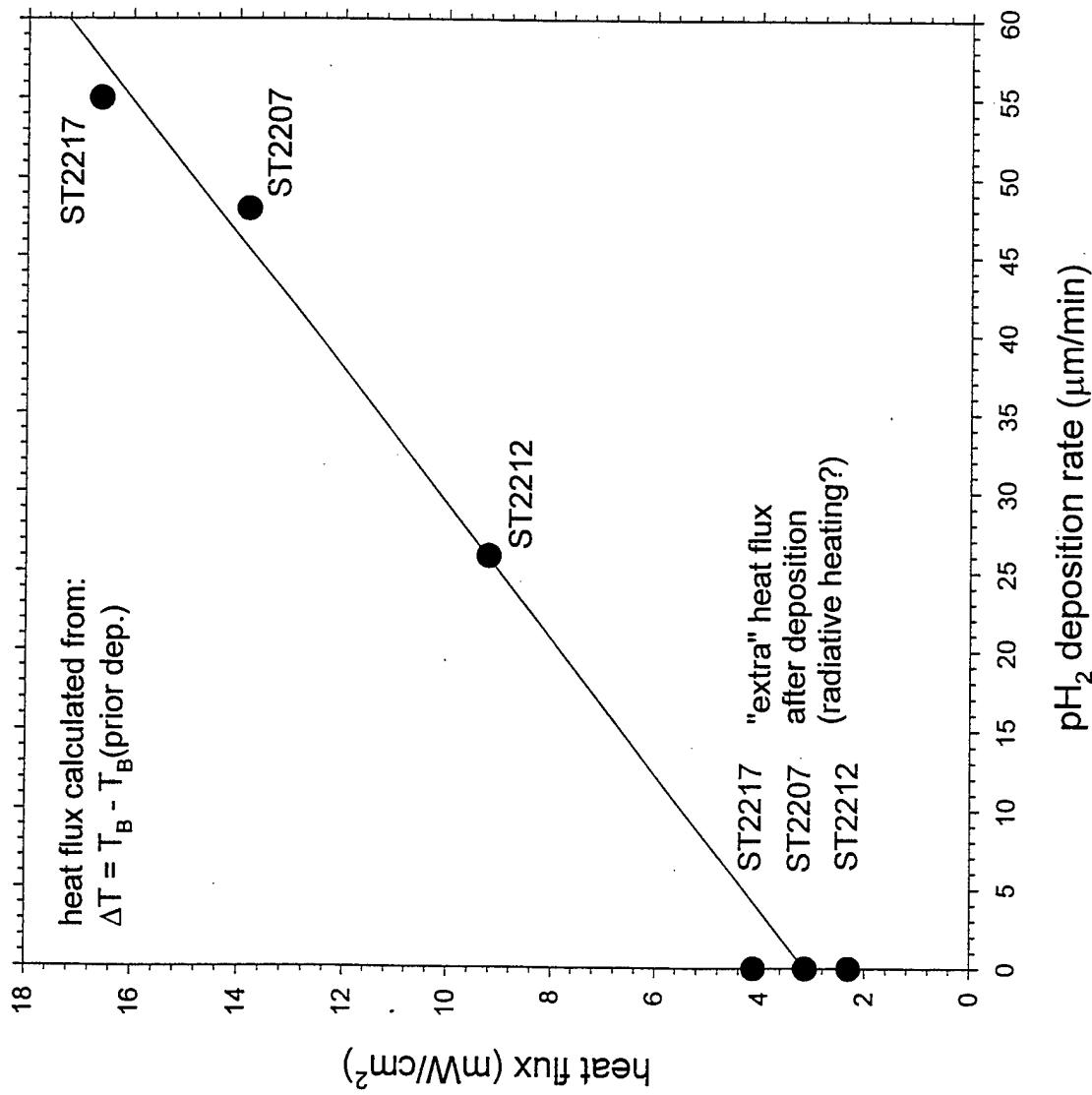
Monitor response of Si diode temperature sensors at positions A and B.

Match observed temperature rises during electrical heating and during depositions to estimate heat fluxes during depositions.

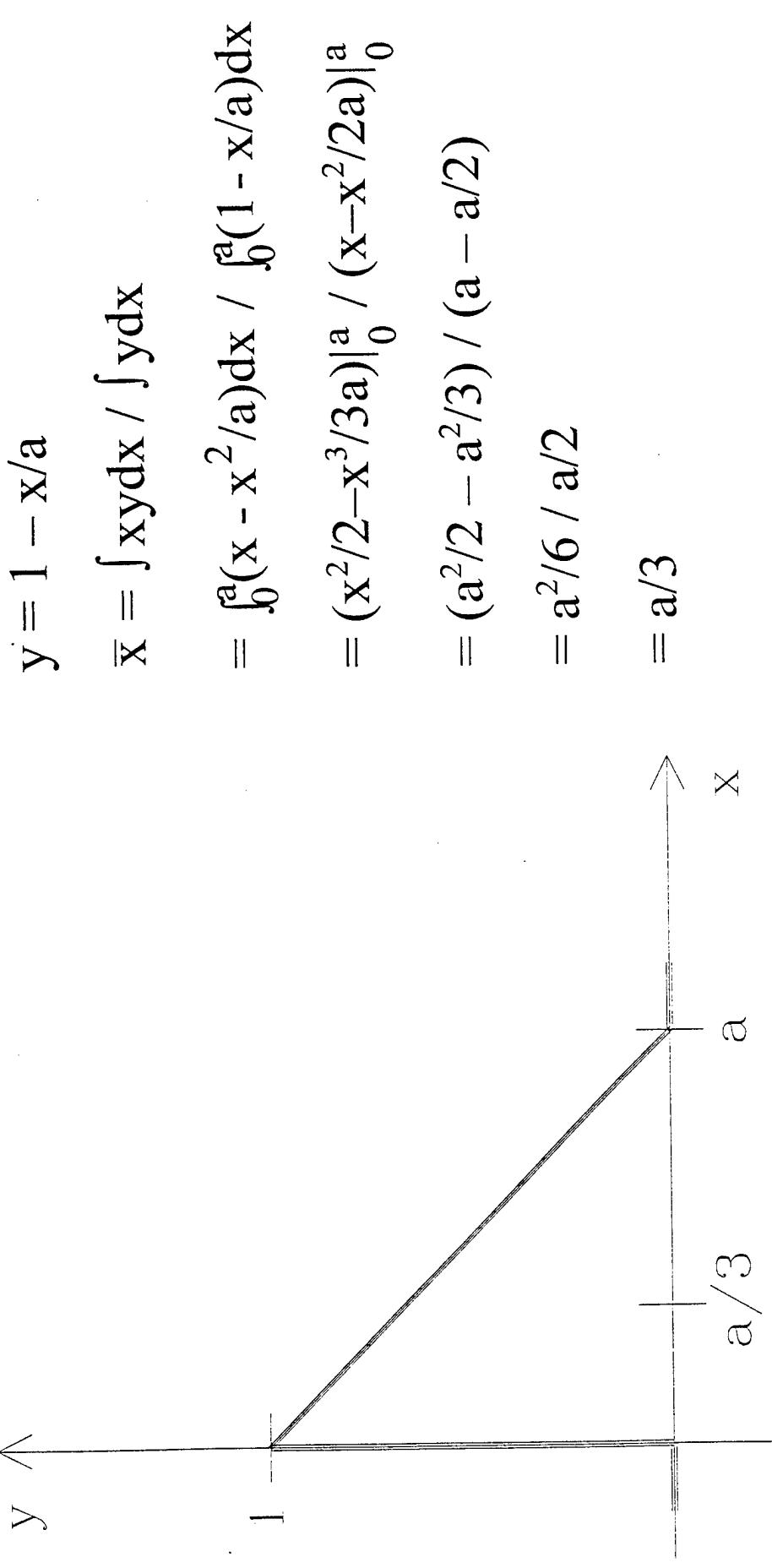
Thermal Response of lHe Cryostat



Calculated Heat Flux vs. pH₂ Deposition Rate



Time-Weighted Average Position of CO Thermometer



Thermal Conductivity of Rapid Vapor Deposited pH₂

Expt.	$[T_{co} - T_B]$ (K)	Δx (cm)	\dot{Q}/A (mW/cm ²)	κ (mW/cm-K)
ST2212	0.61	0.12	9.2	1.8
ST2207	1.19	0.22	13.8	2.6
ST2217	1.74	0.25	16.6	2.4

Expt.	$[T_{co} - T_B]$ (K)	Δx (cm)	\dot{Q}/A (mW/cm ²)	κ (mW/cm-K)
ST2212	0.61	0.12	6.9	1.4
ST2207	1.19	0.22	10.7	2.0
ST2217	1.74	0.25	12.5	1.8

Summary

Absorption spectrum of ~100 PPM CO/pH₂ shows reversible temperature dependent changes which can be used to measure the temperature of the bulk pH₂ during sample deposition.

During a typical rapid deposition ($R \approx 50 \mu\text{m}/\text{min}$), the substrate temperature rises about 1 K, and the pH₂ bulk temperature rises about another 1 K in ~0.1 cm thick samples.

Heat flux during a typical rapid deposition is $\sim 10 \text{ mW/cm}^2$. This value is about 3x larger than the lower limit estimated from the heat of sublimation of solid pH₂.

Calculated thermal conductivities are $\sim 1 \text{ mW/cm}\cdot\text{K}$, about an order of magnitude smaller than previously measured for doped samples grown in an enclosed cell near 10 K.

Our lower thermal conductivities remain unexplained; speculations include:
polycrystalline nature of our samples,
random-stacked close-packed microscopic structure,
systematic errors in our measurements.

Future efforts will include a more careful analysis of possible errors due to radiative heating and other effects.